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DISPOSAL OF WASTES FROM THE CLEANING OF AIRPLANES

L. R. Setter, et al

Environmental Health Center
Cincinnati, Ohio

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DISPOSAL OF WASTES FROM THE CLEANING OF AIRPLANES

by

L. R. Setter, A. S. Goldin, C. Henderson, and M. W. Carter

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ABSTRACT

The pollutional characteristics, including fish toxicity, and the treatability of six airplane cleaning wastes from operations at the Lockbourne Air Force Base were investigated. The waste derived from the use of Airmulso-kerosene-rinse water was less toxic and more readily and inexpensively treated than the waste derived from Gunk-kerosene-water rinse. The high organic pollution and toxicity in the Airmulso waste was effectively reduced with lime and ferric sulfate treatment in less than 2.5 hours. The waste derived from steam-steam cleaner compounds had far less organic pollution and toxic properties than the emulsifier-solvent type wastes, but the high residual alkalinity prevented effective chemical treatment. Of the two steam cleaner compounds, specification No. 3347 produced a waste which was less toxic and had slightly less organic pollution than Formula C (specification No. 14128). The use of both Airmulso-solvent cleaner and steam-steam cleaner Formula C produced a waste which was most high in organic and toxic properties and quite stable to chemical treatment. However, the emulsion could be broken with chlorine treatment and neutralization with acid. The waste derived from a cold water-detergent wash was of intermediate organic pollution and toxicity and could be readily treated by chemical precipitation.

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GENERAL INFORMATION

The studies covered by this report were conducted as a part of the contract between the Air Materiel Command, U. S. Air Force, and the Environmental Health Center, Public Health Service. This agreement provides for the study of certain environmental health problems arising as a result of Air Force operations.

The present study was concerned with wastes resulting from airplane washing operations. Such wastes, in addition to cleaning agents, contain dirt and organic matter and may contain radioactive materials and biological warfare agents.

In essence, the study involved the collection of waste samples, the determination of the pollutional characteristics of the wastes, the investigation of treatment methods necessary prior to discharge into the stream, and a determination of the toxicity to fish of the untreated and treated effluents. The information developed by this study is to be used as one factor in determining the suitability of the individual compounds for the cleaning of airplanes. The waste was produced from operations at the Lockbourne Air Force Base at Columbus, Ohio, during the period September 28, to October 9, 1953.

WASHING COMPOUNDS

Six complete tests were made using various cleaners or combinations, as indicated in table 1. The emulsion cleaners were diluted in the ratio of one volume of cleaner compound to 9 volumes of kerosene, while the alkaline cleaner was diluted in the ratio of 2 ounces per gallon of water before use. Each of the steam cleaners was made up in a 5 per cent solution and fed into the steam line, from which it was applied in a concentration varying between 0.3 and 1.2 per cent.

Table 1 - TYPES AND QUANTITIES OF CLEANERS, WASTE VOLUMES, AND CLEANING TIME

Test No.	Type of Aircraft	Surface Cleaned	Type of Cleaner	Spec. No. of Cleaner	Amount of Cleaner	Amount of Water (Gallons)	Cleaning Time (Minutes)
I	B-47	Entire	Gunk (Emulsion)	AF20015E	50 gal.	2,005	155
II	KC-97*	"	Airmulso (Emulsion)	2844	56 gal.	3,690	180
III	B-47	"	Alkaline	2220AFX	50 gal.	1,780	150
IV**	-	-	-	-	-	-	-
V	KB-29	One wing	Formula C (Steam)	14128A	52.5 lbs.	1,655	33
VI	KC-97	"	"3347" (Steam)	3347	42.5 lbs.	2,350	35
VII	KB-29	"	Airmulso plus Formula C	-	30 gal. 51.3 lbs.	1,965	28

* Forty gallons of kerosene used to wash engines, in addition to water and cleaning compound.

** Test IV re-run as test V, due to equipment failure during washing operation.

WATER SUPPLY

The chemical composition of the waste water can affect treatment methods and also the toxicity of the wastes to fish. The water used in these tests is obtained locally from deep wells. It receives no treatment, other than chlorination, before use. Analyses of water used during the tests showed a pH of 7.5, a soap hardness of 232 p.p.m., and a methyl orange alkalinity of about 360 p.p.m.

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SAMPLING AND GAGING PROCEDURES

The airplanes are washed on a concrete apron measuring about 150 x 175 feet. The apron is sloped toward the center so that all wash and rinse waters drain to a sewered sump. A low weir was inserted at the outlet end of the sump, and the samples collected from the downstream side of the weir by means of a Brittingham pump, with the pumping rate adjusted in proportion to the waste flow.

Due to the construction of the collecting sump and the relatively small rate of flow it was not convenient to measure the volume of wastes at the outlet end of the sump. The wash rack is provided with four water outlets at convenient points. Standard water meters were installed at each of these outlets and readings taken before and after each outlet was used.

Additional sources of wastes entering the collecting sump were from the tanks holding the cleaning compounds and the water tank located on the "Cherry Picker," a truck-mounted mobile unit recently developed by the Air Materiel Command and being tested during this study. In cases where tanks were equipped with gages, these were read and recorded to obtain the amount used in each test. In other cases, the volume used was obtained by manually measuring the depth of the liquids in the container before and after each test.

In order to check on the adequacy of the sampling procedures an alkalinity balance was calculated for each test. The total alkalinity found by laboratory analysis was compared to the total alkalinity calculated on the basis of the constituents used in producing the wastes. The results indicated that the samples were adequately representative of the water "soluble" wastes.

LABORATORY PROCEDURES

The laboratory work included physical and chemical analyses, treatment, and determination of toxicity to fish.

CHEMICAL AND PHYSICAL ANALYSES

The following chemical and physical determinations were made in accordance with the procedures given in "Standard Methods," 9th Edition (1): total solids, total volatile solids, total fixed solids, total suspended solids, volatile suspended solids, fixed suspended solids, hydrogen-ion concentration (pH), total alkalinity, immediate chlorine demand, 15-minute chlorine demand, residual chlorine, dissolved oxygen (Winkler method), and 5-day 20° C. biochemical oxygen demand. Oxygen consumed, turbidity, relative optical transmittance and sludge and scum volumes were determined as follows:

Oxygen Consumed: Aliquots were refluxed for 2 hours in a 300 ml. flask containing 25 ml. of 0.25N $K_2Cr_2O_7$, 75 ml. of conc. H_2SO_4, 1 g. Ag_2SO_4 catalyst, and distilled water to make a total volume of 150 ml. After cooling, the residual oxidant was determined by titration with ferrous ammonium sulfate. The results are reported in p.p.m. of oxygen equivalent to the dichromate consumed. The Ag_2SO_4 was omitted where significant quantities of chloride were present.

Turbidity: The light transmission of a sample in a 20 mm. cell was measured in a Photo-Volt Lumetron Colorimeter, Model 402-E, using a 515 mμ filter. Suspensions of infusorial earth in distilled water were used to prepare a calibration curve. The results are reported in p.p.m. as infusorial earth.

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(1) Standard Methods for the Examination of Water and Sewage A.P.H.A., 9th Edition, 1946

Relative Optical Transmittance: Light transmittance was measured in a Photo-Volt Lumetron Colorimeter, Model 402-E, at 515 mμ, using a 20 mm. absorption cell.

Sludge and Scum Volume: After removing most of the clarified liquid, the remaining volume of sample was transferred to a graduated cylinder and allowed to settle for two hours. The volume of sludge or scum was then read from the cylinder and calculated as a percentage of the total volume of the sample.

TOXICITY DETERMINATIONS

The methods used in the bioassays were essentially those outlined by Doudoroff et al (2). Tests were performed at an average temperature of 22°C. with a maximum fluctuation of 2°C. Fathead minnows (Pimephales p.promelas) from 1-1/2 to 2-1/4 inches, total length, were used in all tests. These are of intermediate tolerance (comparable to bass and other warm water game species) to toxic materials, easily adaptable to laboratory aquaria and of wide occurrence naturally. Minnows used in these experiments were obtained from the Ohio State Hatchery at Newtown, Ohio. They were acclimated in the water used in the experiments for at least one week and were not fed for 48 hours before using.

Preliminary experiments indicated that the materials to be tested were more toxic in soft than in hard water. The dilution water used in most of the experiments was prepared from 19 parts dechlorinated distilled water and 1 part natural hard water obtained from springs at the Newtown Hatchery. This mixture simulated a natural soft water and was easily reproducible in the laboratory. Some experiments were carried out using the straight hatchery

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(2) Doudoroff et al
"Bioassay Methods for the Evaluation of Acute Toxicity of Industrial Wastes to Fish."
Sew. & Ind. Wastes, Vol. 23, No. 11, 1380 (1951).

water which was somewhat similar to the water used on the wash racks at the Lockbourne Air Base.

The characteristics of the waters used were as follows:

	Prepared	Hatchery	Lockbourne
pH	7.4-7.6	7.7-8.0	7.8
Alkalinity	16-20	300	360
Hardness	18-20	248	232

In conducting the experiments dilutions were prepared on a percentage by volume basis. Necessary quantities of effluent were added to water in the test containers to make up the appropriate dilutions. Fish were then transferred from the acclimatizing aquaria directly to the prepared dilutions. Exploratory tests were set up using 2 fish in each test for a wide range of dilutions, such as 100, 10, 1, and 0.1 percent. Death of the fish was noted and thus the critical range established.

Subsequent tests were made on concentrations within the established critical range. Appropriate series of dilutions were prepared on a logarithmic scale (e.g., 10, 5.6, 3.2, 1.8, and 1.0 percent). Four fish were added to six liters of solution in each bottle. Duplicates were prepared for each dilution, as well as for controls, consisting of the dilution water only. Initial temperature, dissolved oxygen, pH, and alkalinity were recorded. Observations were made on each series of experiments for a total of 96 hours or more. The number of fish surviving, the dissolved oxygen content, and water temperature were recorded at intervals of 24, 48, and 96 hours. Alkalinity and pH determinations were made at the end of 96 hours. Where all fish in a container were dead before 24 hours, the time of death and the D.O. content was noted. From the observations made, the approximate median tolerance limit, TLm (concentration in which 50 percent of fish survive), was calculated

at 24, 48, and 96 hours. This was done by plotting the percent survival above and below 50 percent on a log scale against percentage concentration on an arithmetic scale. From a straight line graphical interpolation, the percent concentration at which 50 percent of fish survive was determined. The maximum concentration at which there was 100 percent survival was also noted.

CHARACTERISTICS AND COMPOSITION OF WASTES

The total amount of wastes taken during each of the tests varied from 25 to 40 gallons, collected in 5-gallon carboys. Observations and chemical analyses indicated a similarity among individual carboys from a particular test. This being the case, all the waste from each operation was mixed in a tank to make a single sample for test purposes. The chemical and physical characteristics of the raw wastes are shown in table 2.

The inorganic content of the wastes is indicated by the results for fixed solids and alkalinity. For these parameters, Wastes I, II, and III have values not very much greater than the values for the water alone. On the other hand, Wastes V, VI, and VII, all of which contain large quantities of alkaline steam-cleaner compounds, have much higher values of these constituents - 1,700 to 2,500 p.p.m. total fixed solids, pH between 9.5 and 10, and 1,000 to 1,500 p.p.m. total alkalinity. Waste III is also from an alkaline cleaner, but it was used in such a low concentration that it did not materially affect the inorganic content of the sample.

The organic pollutional load is measured chiefly by the five-day biochemical oxygen demand (B.O.D.), by the acid-dichromate oxygen consumed value (O.C.), the chlorine demand, and, to a lesser extent, by the volatile solids content. For these parameters, the three wastes using organic emulsifying agents (I, II, and VII) have much higher values than do Wastes III, V, and VI. Again, it must be realized that Waste III was produced by a cleaner containing some kerosene, but the concentration of cleaner used in Waste III was very low. The value of total volatile solids in Wastes I, II and VII may be low, due to loss of volatile constituents (kerosene) at the temperature of drying (103°C.). The relatively high values of volatile solids in the wastes may be attributed to organic matter, such as grease, oil, and insect bodies,

Table 2 - RESULTS OF ANALYSES OF RAW WASTES

Waste No.	I	II	III	V	VI	VII
Cleaner	Gunk	Airmulso	2220AFX	14128	3347	Airmulso + 14128
Total Solids, p.p.m.	1175*	718*	943	3035	2255	3431*
Fixed, p.p.m.	480	367	541	2500	1714	2478
Volatile, p.p.m.	695	351	402	515	541	953
Suspended solids, p.p.m.	170	102	156	193	444	198
Fixed, p.p.m.	60	40	107	129	310	74
Volatile, p.p.m.	110	62	49	64	134	124
Turbidity, p.p.m.	1400	500	420	1000	720	7000
pH	8.1	7.85	8.0	9.85	9.6	9.8
Alkalinity to						
pH 8, p.p.m.($CaCO_3$)	10	0	0	500	250	425
pH 4, p.p.m.($CaCO_3$)	460	400	510	1460	990	1450
Oxygen Consumed, p.p.m.	2780	2000	700	1070	750	10,300
5-day B.O.D., p.p.m.	810	600	330	200	90	3300
Chlorine Demand						
15-minute, p.p.m.	37	46	10	12	12	43
Immediate, p.p.m.	20	10	5	10	5	20

* Exclusive of volatile solvent losses at the drying temperature (103° C.)

removed from the aircraft during cleaning.

All the wastes are rather strong in pollutional load as measured by the B.O.D. An average demand for a weak domestic sewage is in the order of 200 p.p.m., a value equalled or exceeded by all the wastes except number VI.

Wastes I, II and VII consisted of emulsions, which, when fresh, were light grey in color with a distinct kerosene odor. Upon aging, these wastes developed a scum on their surfaces and gave off a rather unpleasant odor. When aged for approximately six weeks, the emulsions were partially broken in Wastes I and II, and entirely broken in Waste VII. The emulsion in Wastes I and II became less opaque with resulting scum formation. Waste III was fairly clear originally, but upon aging some material settled out, leaving a very clear supernatant.

Wastes V and VI were originally dark in color due to the presence of paint which was washed off the aircraft during washing operations. These wastes became darker upon aging and had both sludge and small scum formations.

Some floating material was present in Wastes I, II, and VII. Since it did not mix readily with the aqueous phase of the sample the material was removed by skimming prior to the analyses shown in table 2. Some of the characteristics of the skimmings were determined.

The skimmings separated into three layers consisting of a top layer of oil, a middle layer of light sludge, and a bottom layer of heavy sludge. The volume of each layer was observed and the oil removed. The sludges were then treated with sufficient sulfuric acid to lower the pH value to between 1.5 and 3.0. This acidification resulted in a rapid separation of the sludge into a top layer of oil and a bottom layer of water with some sludge between these phases. The results of these tests are presented in table 3.

Table 3 - BEHAVIOR OF SKIMMINGS FROM RAW WASTES

	WASTE I	WASTE II	WASTE VII
Total sample - gals.	30	40	28
Untreated skimmings after 24-hour settling:			
Total volume, ml.	1,740	1,350	350
Upper layer	425	235	180
Middle layer	40	190	90
Lower layer	1,275	925	80
Acidified sludges after 2-hour settling:			
Total volume, ml.	1,335	1,125	175
Upper layer	265	170	70
Middle layer	135	145	25
Lower layer	935	810	80
Total skimmings:			
Oil - %	40	30	70
Water - %	55	60	25
Total Waste:			
Oil - %	0.61	0.27	0.24
Sludge - %	0.12	0.10	0.02
Burning of skimmings after acidification and water removal:			
Specific gravity	0.82	0.85	0.85
In open crucible - %	99.4	91.9	89.1
@ 650° C. for 1/2 hr.	99.8	98.8	99.5

The separable oil and sludge content of the total waste is relatively small. The skimmings themselves, however, contain between 30 and 70 percent oil and from 25 to 60 percent water. No data were secured on the combustibility of these skimmings prior to removal of the water. After acidification and removal of the water by gravity separation it was found that 89.1 to 99.4 percent of the residue would burn off in a crucible ignited in open air. When ignited in a muffle at 650° C. for one-half hour a total loss of from 98.8 to 99.8 percent occurred.

WASTE TREATMENT

Three methods of treatment to reduce the fish toxicity and pollutional potential of the wastes were used, namely coagulation, aeration and chlorination. The relation between the B.O.D. and O.C. is also indicative of the applicability of biological treatment methods. Since the results of the fish toxicity studies were in part used as a guide in developing the treatment methods such studies are referred to in this section. A more detailed discussion of the fish toxicity work is presented in a later section of the report.

COAGULATION

Coagulation was used as a method of treatment for all the wastes. Sulfuric acid, ferric sulfate, lime, and trisodium phosphate were added, either singly or in combination. Wherever practical, a precipitation of ferric iron at an alkaline pH was used, since previous experience had shown that this combination was useful in removing a large part of fission-product radioactivity.

The criteria used in evaluating this method of treatment were: reduction of turbidity, reduction of oxygen demand, reduction of fish toxicity, and production of a minimum amount of sludge. Median tolerance limit values in the fish toxicity test may be low, since some of the fish deaths seemed to be caused by lack of oxygen, rather than by the presence of toxic materials. Details of the more successful coagulation methods are presented in table 4.

Wastes I, II, and III responded to treatment by chemical coagulation. Waste I required contact with sulfuric acid to break the emulsion, followed by addition of ferric salt and coagulation of the latter by lime. The final effluent was substantially clear, the oxygen demand had been largely removed, and the fish toxicity markedly reduced. The acid-iron sulfate-lime treatment was partially effective for Waste II but the simple treatment of adding lime,

Table 4 - RESULTS OF TREATMENT OF WASTES BY COAGULATION

Waste Number	Treatment		Characteristics					
			pH	Turbidity (p.p.m.)	B.O.D. (p.p.m.)	O.C. (p.p.m.)	TIm at 96 hrs. (%)	Sludge Vol. at 2 hrs. (%)
I	1. H_2SO_4, 9 meq/l 2. 30 minute stir 3. $Fe_2(SO_4)_3$, 0.8 meq/l 4. CaO, 300 p.p.m. 5. 30 minute stir 6. 2 hr. settling	Initial Final % Reduction	8.1 6.7	1400 10 >99	810 250 69	2780 1015 64	2.5 53	1.2
II	1. CaO, 400 p.p.m. 2. $Fe_2(SO_4)_3$, 1.0 meq/l 3. 20 minute stir 4. 2 hr. settling	Initial Final % Reduction	7.85 10.6	500 <10 >98	600 90 85	2000 575 71	5.0 46	3.0
III	1. $FE_2(SO_4)_3$, 2.0 meq/l 2. Na_3PO_4, 2.0 meq/l 3. 30 minute stir 4. 2 hr. settling	Initial Final % Reduction	8.0 6.9	420 <10 >97	330 195 41	700 460 34	15 29	4.6
V	1. H_2SO_4, 20 meq/l 2. 20 minute stir 3. Na_3PO_4, 3.3 meq/l 4. $Fe_2(SO_4)_3$, 3.0 meq/l 5. CaO, 140 p.p.m. 6. 2 hr. settling	Initial Final % Reduction	9.85 7.7	750 375 50	200	1070	5.6	8.0
	1. $Fe_2(SO_4)_3$, 20 meq/l 2. 20 minute stir 3. 1 hr. settling	Initial Final % Reduction	9.85	750 85 87	200	1070	5.6	26 (1 hr.)

Table 4 - RESULTS OF TREATMENT OF WASTES BY COAGULATION (Cont'd.)

Waste Number	Treatment	Characteristics						
			pH	Turbidity (p.p.m.)	B.O.D. (p.p.m.)	O.C. (p.p.m.)	TLm at 96 hrs. (%)	Sludge Vol. at 2 hrs. (%)
VI	1. CaO, 700 p.p.m. 2. 20 minute stir 3. Na_3PO_4, 1.1 meq/l 4. $Fe_2(SO_4)_3$, 1.0 meq/l 5. 20 minute stir 6. 2 hr. settling	Initial Final % Reduction	9.6 10.8	720 205 72	90	750 325 56	28	10
VII	1. H_2SO_4, 6 meq/l 2. 30 minute heating 3. 2 hr. settling	Initial Final % Reduction	9.8 9.1	7000 130 98	3300	10,300	1.35	15
	1. H_2SO_4, 36 meq/l 2. 20 minute stir 3. 24 hr. contact 4. Scum removed 5. CaO, 225 p.p.m. 6. 20 minute stir 7. 1.5 hr. settling	Initial Final % Reduction	9.8 8.8	7000 210 97	3300	10,300	1.35	11 11

followed by a small amount of ferric sulfate gave better results. This treatment removed practically all of the turbidity, about three-fourths of the oxygen demand, and reduced the fish toxicity by a factor of 9. It was found that Waste III could be coagulated with the addition of a relatively small amount of ferric sulfate and sodium phosphate. Almost all the turbidity and about 40 per cent of the oxygen demand were removed. The TL_m was raised from 15 to 29 per cent. Similar treatments of Wastes V and VI were not very satisfactory. Either excessive chemical dosages had to be used, or the effluents were of poor quality. Waste VII had been subject to excessive aging prior to treatment so a synthetic waste of comparable composition was prepared for treatment studies. Cursory studies of the aged waste indicated that a substantial reduction in turbidity resulted by lowering the pH with a small amount of sulfuric acid. The addition of larger amounts of acid with or without some lime was without benefit.

AERATION

The high organic content of the wastes indicates that aeration might prove an effective treatment. Unfiltered, compressed air from the laboratory supply was passed through 2-liter samples of each waste for a period of 18.5 hours. The criteria used in evaluating this treatment were the dissolved oxygen content, optical transmittance, and toxicity to fish.

The results are given in table 5. All of the wastes, except VII, became less toxic to fish, and three of the wastes (I, II, and III) were clarified, as shown by the increase in optical transmittance.

The aeration experiments were exploratory in nature. Therefore, determinations such as oxygen demand were not run and only rough, exploratory fish toxicity tests were made. From the results obtained in these

experiments, it was concluded that aeration markedly improved all the wastes except Waste VII. However, as Waste VII appeared to present the most difficult treatment problem, the method was discontinued.

CHLORINATION

Chlorine consumption curves for the wastes were obtained by adding chlorine water to a portion of each sample, mixing, and determining residual chlorine at intervals up to two hours. The initial chlorine dosage was 88 p.p.m. for Wastes I, II, and VII; and 44 p.p.m. for Wastes III, V, and VI. The chlorine consumption data are shown in table 6. It is apparent from the data that those wastes containing organic emulsifier-type cleaners have a relatively high chlorine demand, while the alkaline and steam-cleaner compound wastes have low chlorine demands.

Using these chlorine demand data as a guide, two-liter samples of each waste were chlorinated. Ninety p.p.m. of chlorine was added to each of Wastes I, II, and VII; and 45 p.p.m. to each of Wastes III, V, and VI. After a 2-hour contact time the residual chlorine was destroyed with sodium thiosulfate. Optical transmittance and toxicity to fish were used as parameters by which the usefulness of the treatment could be judged. The transmittance values were also determined after an eighteen-hour settling period.

The results of these experiments are summarized in table 7. The data show that all the wastes were clarified and the toxicity decreased. The improvement in Waste VII being especially large. The marked improvement in optical transmittance with this waste was caused by a breaking of the emulsion into a relatively clear liquid phase and a white scum. The latter after a two-hour settling period, amounted to 9.3 per cent by volume.

Because of the favorable results obtained by chlorinating Waste VII, further exploratory tests were made on this waste to determine optimum

Table 5 - RESULTS OF TREATMENT OF WASTES BY AERATION

Waste No.		pH	D.O. - p.p.m.	Transmittance %	TL_m (96 hr.) %
I	a	7.4	2.4	28.5	2.5
	b	7.2	4.2	56.0	>10
II	a	7.4	2.6	25.0	5.0
	b	7.2	5.6	59.0	>10
III	a	7.3	0.0	69.5	15
	b	9.0	5.8	83.0	>32
V	a	9.8	4.0	24.5	5.6
	b	9.6	6.2	24.5	>18
VI	a	9.5	2.6	36.5	28
	b	9.2	5.2	36.0	>42
VII	a	9.9	1.6	10.5	1.35
	b	9.5	2.4	2.0	<3.2

a - Preceding aeration b - Following aeration

chlorine dosage. It was found that larger doses of chlorine served to break the emulsion more quickly and more completely, with little improvement for dosages above 150 p.p.m. Cl_2.

On the basis of the results of these exploratory tests, an eighteen-liter sample of Waste VII was treated with 145 p.p.m. of chlorine. The sample was left in contact with the chlorine for a total of 65 hours, aliquots being taken at intervals for determination of pH, optical transmittance, residual chlorine and the sludge volume. The data showed that with prolonged contact the emulsion was more completely broken and the sludge was reduced in volume.

Table 6 - CHLORINE DEMAND OF RAW WASTES

Waste No.	Chlor. Dose p.p.m.	Chlorine Demand - p.p.m.					
		0 min.	15 min.	30 min.	60 min.	90 min.	120 min.
I	88	37	54	60	70	73	76
II	88	26	49	56	61	61	70
III	44	9	18	21	25	29	32
V	44	6	16	17	22	28	31
VI	44	7	16	21	25	28	31
VII	88	36	63	75	81	82	83

Fish toxicity tests on the clear water waste showed a median tolerance limit (TL_m) of 19 per cent, as compared with the original value of 1.35 per cent.

SYNTHETIC WASTES

It was indicated that biological changes had occurred in the wastes on aging. In addition, it was considered likely that some chemical changes, such as hydrolysis had occurred. For these reasons, mixtures consisting only of cleaning agent in Cincinnati tap water, were prepared to simulate Wastes I, II and VII, since the visible changes in these wastes were more extensive than in the others. The synthetic wastes were made up with concentrations of cleaning agents approximately equal to those used in the original tests.

In general, the results of preliminary tests on synthetic wastes I and II were similar to those obtained from treatment of wastes taken under actual operating conditions.

However, since Waste VII had undergone considerable physical alteration on storage, the studies of this waste was made primarily on a synthetic waste consisting of 1.8 ml of 10% Airmulso in kerosene solvent and 3 grams of Formula C diluted in a liter of Cincinnati tap water. This mixture had a pH

Table 7 - RESULTS OF TREATMENT BY CHLORINATION
(90 p.p.m. Cl_2 added I, II and VII; 45 p.p.m. Cl_2 added to Wastes III, V and VI.)

Waste No.	Treatment Time	pH	Transmittance %	TLm (96 hr.) %
I	Initial	8.0	31.5	2.5
	2 hr.	6.9	34.0	10
	20 hr.	7.7	38.5	
II	Initial	7.9	32	5.0
	2 hr.	7.0	39	5.6
	20 hr.	7.7	44.5	
III	Initial	7.2	79.5	15
	2 hr.	7.2	83.0	>32
	20 hr.	8.1	92.0	
V	Initial	9.6	33.5	5.6
	2 hr.	9.6	37	14
	20 hr.	9.7	45	
VI	Initial	9.2	35	28
	2 hr.	9.2	40.5	35
	20 hr.	9.2	49.5	
VII	Initial	9.4	2.5	1.35
	2 hr.	9.3	36.5	24
	20 hr.	9.4	89.5	

of 10.9, an alkalinity of 1,180 p.p.m. ($CaCO_3$)and an O.C. of 15,400 p.p.m. Both the pH and O.C. are somewhat higher than found in the Lockbourne Waste VII.

Acidification with acid and ferric sulfate treatments similar to those of Waste I or II was not effective with large chemical dosages. Lime treatment with or without tri-sodium phosphate was also ineffective. Chlorination at a high pH (10.9) was ineffective while chlorination at low pH (3.1) was only partially effective. However, it was found that the synthetic waste emulsion could be broken in 4 or more hours contact merely by adjusting the pH to a rather critical range, with an optimum of 6.8 to 7.0. Due to the high alkalinity of the waste a dose of 600 to 700 p.p.m. of H_2SO_4 was required for pH adjustment.

More complete emulsion breaking was obtained in a shorter time over a less critical pH range if the waste was first chlorinated with 100 to 200 p.p.m., prior to pH adjustment with 500 to 600 p.p.m. of H_2SO_4. For example, the addition of 100 p.p.m. of Cl_2 and 590 p.p.m. of H_2SO_4 resulted in a pH of 6.9. After 2 and 18 hours contact the transmittance increased from an initial value of 3.5% to 72 and 92%, respectively. The volume of floating scum, which was 14.7% after two hours, compacted to 11.8% after 3 hours. The oxygen consumed value of the water waste was 740 p.p.m. after 18 hours or a 95% reduction, and the fish toxicity decreased over 18 fold for the 18-hour contact period or from an initial TL_m (96 hrs.) of 0.56% to over 10%.

FISH TOXICITY STUDIES

In order to evaluate the possible damage to aquatic life, bioassays were performed on effluents from the six different washing methods previously described. The comparative toxicity of these effluents will assist in determining which washing method may be satisfactory from the standpoint of disposal into a variety of receiving waters without detrimental effects to fish life. Bioassays were performed on each of the treated effluents in order to determine the effectiveness of the treatment methods in reducing initial toxicity. These tests were also made on the original cleaners used in the washing process.

Table 8 gives a summary of results of the bioassays, showing the 96-hour median tolerance limits (TL_m) and the maximum concentration of solution in which there was 100% survival of fish for the raw wastes, the treated wastes, and the waste components. These results are based on the toxicity of the materials in soft (prepared) water with no aeration or oxygenation. In evaluating the figures for toxicity certain factors must be considered, namely, the time between collection and toxicity determination, the kind of water used in the preparation, and the possibility of loss of fish due to oxygen depletion.

RAW OR UNTREATED WASTES

The initial toxicity was determined two to four weeks after the wastes were collected. It was indicated that the raw wastes decreased in toxicity upon aging. Experiments repeated with Wastes I and V approximately two weeks after the initial tests were made indicated the toxicity was reduced approximately one-half during this period. The 96 hr. TL_m of Waste I was increased from 2.5 to 4.2% and of Waste V from 5.6 to over 10 percent.

Table 8 - SUMMARY OF RESULTS OF BIOASSAYS ON RAW WASTES AND CLEANING COMPOUNDS

Determination	Waste Number					
	I	II	III	V	VI	VII
TLm at 96 hours (raw) - %	2.5	5.0	15	5.6	28	1.35
TLm at 96 hours (treated) - %	53	46	29	—	<32	19
100 percent survival at 96 hours (raw) - %	1.0	3.2	10	3.2	24	0.56
100 percent survival at 96 hours (treated) - %	42	32	18	—	<32	10
Cleaner	Gunk*	Airmulso*	2220AFX	14128	3347	Airmulso* and 14128
TLm at 96 hours - %	0.0013	0.0029	0.0042	0.024	0.022	-
100 percent survival at 96 hours - %	0.00056	0.0018	0.0032	0.018	0.010	-
Cleaner mix at 1 to 9 ratio	Gunk: Kerosene	Airmulso: Kerosene	-	-	-	-
TLm at 96 hours - %	0.0056	0.013	-	-	-	-
100 percent survival at 96 hours - %	<0.0032	<0.0056	-	-	-	-

* In practice these cleaners are mixed 1:9 on a volume basis with kerosene before use.

The raw wastes contained a hard water while the dilution water was soft. Consequently, the test dilutions contained a varying degree of hardness. Based on experimental data comparing the toxicity of some of the waste components in soft and hard water, as shown in table 9, the raw wastes appear somewhat more toxic in a soft water.

All of the wastes indicated some degree of oxygen depletion in the test dilutions. However, the degree of depletion appeared to have little or no effect on fish mortality and consequently on the toxicity values shown in table 8. A possible exception to this was in Waste III in which very low oxygen values were present after the death of the fish. It was decided, however, not to use aeration or oxygenation in these experiments to maintain adequate D. O. values since the use of either compressed air or pure oxygen might affect the toxicity values to a greater degree than would a slight oxygen deficiency in some of the test dilutions. For example, a 10% dilution of Waste I which had killed fish very quickly, in the absence of adequate dissolved oxygen, when allowed to stand overnight, then aerated, had no apparent effect on fish. It thus appeared that either a chemical or biological oxidation had decreased the toxicity of the waste. These observations initiated exploratory studies on the treatment of wastes by oxidation methods.

TREATED WASTES

The bioassays on treated wastes were performed immediately after obtaining the treated effluents. The treatments, however, were on wastes collected from one month to six weeks previously and no doubt the initial toxicity was somewhat reduced. The treatments appeared quite effective both in improving physical and chemical characteristics and in reducing

Table 9 - RELATIVE TOXICITY OF CLEANERS IN HARD AND SOFT WATER
(Exploratory tests only)

Cleaner	Dilution Water	96-hour TL_m - %
Gunk	Hard	0.011
	Soft	0.0056
Airmulso	Hard	0.014
	Soft	0.014
Formula C	Hard	> 0.056
	Soft	0.028
"3347"	Hard	0.042
	Soft	0.021

the toxicity to fish. Fairly adequate treatments from the toxicity standpoint were obtained from Wastes I, II, III, and VII. Waste VI, while improved greatly in appearance and other characteristics, was not improved from the toxicity standpoint. Waste V was similar to Waste VI but no adequate treatment was determined for it.

The toxicity values in Table 8 were obtained from dilutions with soft water. It was not determined what effect the use of a hard dilution water may have on the test. As chemical treatment changed these effluents in chemical complexity, it is not expected that the hard water used in the raw wastes would have altered the toxicity assay. There was considerable oxygen demand in the low dilution tests of some treated effluents. Reasonably definite fish mortalities due to oxygen depletion were noted in the low dilutions of effluents from I, III, and VII. When oxygen was maintained in I and III through aeration, all fish survived concentrations of 56% effluent.

Exploratory bioassays were made on all of the raw wastes after first aerating with compressed air for 18.5 hours, as shown in table 5. The toxicities of all of the wastes, with the possible exception of VII, were re-

duced considerably.

Exploratory bioassays were also made on the raw wastes after chlorination, as given in table 7. This treatment (2 hours) appeared quite effective in reducing toxicity and in some cases clarifying the effluent. Toxicity was reduced in all wastes to some degree and very favorably in Waste VII.

Exploratory bioassays were made on a synthetically prepared material comparable to Waste VII. The synthetic waste appeared more toxic than the original raw waste, having a 96-hour TL_m of 0.56% as compared to 1.35% in the raw waste. The synthetic waste was chlorinated with 100 p.p.m. Cl_2 and the pH adjusted to 6.9. This treatment caused the emulsion to break and the clear supernatant was found to have a 96-hour TL_m above 10%, or over an 18-fold decrease in toxicity.

WASTE COMPONENTS

Dilutions of the emulsifiers, solvent-cleaners, and alkaline cleaner compounds were prepared for a determination of fish toxicity on the component parts of the wastes. Generally a stock suspension on 1% of each of the component materials in soft water was prepared and appropriate dilutions in soft water were made from the stock. The bioassays were started immediately upon preparation of the test dilutions. The results of these tests are included in table 8. Since some experiments (table 9) showed that component materials were as toxic or more so in soft water than in hard, the TLm values of the components shown in table 8 are probably representative of the maximum toxicity of these materials. While there was some oxygen depletion in the experimental dilutions the effect was not enough to cause any fish mortality.

In comparing the toxicity of a waste with that of the cleaner components in similar concentration, it appears that the latter are substantially more toxic. The comparison for each of the wastes is shown in table 10, and indicates a detoxification on storage, use of different water, and other factors.

Table 10 - RELATIVE TOXICITIES OF WASTES AND COMPONENTS

Waste No.	Component		Toxicity - 96 hr. TL_m			Relative Toxicity Ratio Actual/Calc.
	Cleaner	Conc. in Waste %	Of Component %	Of Waste Calculated %	Of Waste Actual %	
I	Gunk Mix	2.5	0.0056	0.224	2.5	11
II	Airmulso Mix	1.52	0.013	0.85	5	6
III	Alkaline	0.042	0.0042	10	15	1.5
V	Formula C	0.381	0.024	6.3	5.6	0.9
VI	"3374"	0.216	0.022	10	28	2.8
VII	Airmulso mix plus FormulaC	1.52 .313	0.013) 0.024)	0.76**	1.35	1.8
VIIS*	"	"	"	0.76**	0.56	0.7

* Synthetic Waste VII

** The toxicity of Formula C in waste was calculated to contribute 10% of the total toxicity.

DISCUSSION

The toxicity and pollutants in a waste and the treatability will vary, depending upon the concentration of cleaning agent. In this respect the collection of wastes at Lockbourne, while several pieces of equipment were in use, may be considerably different following a standardization of the washing and rinsing procedures. The nonuniformity of washing procedure is indicated by the varying amounts of water used. For example, 3,690 gallons of water were used in washing a KC-97 plane to produce waste II, whereas, 2,350 gallons of water were used to wash only one wing of a similar plane in producing Waste VI. Had the entire plane been washed the volume of waste water would presumably be at least twice as much as that used in producing Waste II. Similarly, 1,965 gallons of water were used for washing only one wing of a B-29 in producing Waste VII as compared to the 2,000 gallons for an entire smaller plane (B-47) or 3,690 gallons for an entire large plane (C-97). Certainly these volume factors should be considered in evaluating the overall choice of agents on the basis of plane decontamination, pollutional aspects, and treatability or decontamination of wastes.

Another aspect of the problem of airplane cleaning waste disposal is the possible alteration of cleaning agents by formulations, the specifications of which are based on performance only. Major formulation could materially alter the toxicity, pollutional load and treatability of the resulting wastes. In this respect it would be desirable to limit the types and concentrations of wetting agents, sequestering agents, syndets or alkaline detergents permitted in a cleaner in order that the characteristics of the cleaners remain relatively constant from year to year.

In this study little attention was given to the ultimate disposal of sludges or floating matter. In general, the use of an emulsion type

cleaner will, upon settlement, cause some separation of solvent. In fact there is some suspicion that oil was lost in collecting the Lockbourne samples. With adequate plant facilities the floating oil could be readily removed by skimming and purified for reuse or the crude oil, with or without floating sludge, could be readily burned by incineration or other means.

In computing non-toxic dilutions for the disposal of the raw or treated wastes into a variety of receiving waters certain safety factors should be applied:

(1) As fathead minnows are organisms of intermediate tolerance and the TL_m values only measure partial survival, it is necessary to apply a safety factor of at least 10 to assure the complete survival of all aquatic organisms.

(2) The TL_m values for the raw wastes were obtained from effluents which had aged for several weeks. Experiments indicated that the toxicity of these wastes had decreased. Therefore an additional safety factor of 2 or more should be applied to account for increased toxicity in the fresh wastes.

(3) It was indicated that the wastes were more toxic in soft than in hard water. If extremely soft water is used in the washing operations it probably is necessary to apply an additional safety factor of 2.

In this series of experiments the toxicity values for the waste components (Gunk, Airmulso, Alkaline and Steam cleaners) are considered more accurate than those for the raw wastes. It may be preferable to compute safe disposal dilutions directly from the TL_m values of these materials and their percentage composition in the waste, using applicable safety factors.

SUMMARY AND CONCLUSIONS

Studies of six airplane cleaning wastes were made to determine their pollutional characteristics and suitable methods of waste treatment. Besides the usual parameters of pollution, bioassays were made to measure fish toxicity. Two of the wastes were from the use of solvent-emulsifier cleaners, two from the use of steam-steam cleaner compounds, and one from the use of a cold water-detergent wash. The latter waste (III), although appearing to be one of the least toxic to fish and being readily treated by chemical means, was stated by the Air Force to be unsatisfactory for cleaning airplanes.

The wastes from solvent emulsifiers contained Gunk-cleaner (Waste I) and Airmulso cleaner (Waste II), in which one part of emulsifier in nine parts of kerosene was used as a spray, followed by a cold water rinse. The volume of rinse water used produced a waste emulsion of high organic pollutants containing 1.5 to 2.5 percent solvent cleaner. For an equal concentration of solvent cleaner in the waste the pollutioncl characteristics (including fish toxicity) of the two wastes were comparable, but the component materials indicated that in soft water, the Gunk-solvent was twice as toxic as the Airmulso-solvent. The Airmulso-kerosene waste (II) was much more readily treated than the Gunk-kerosene waste. Treatment of Waste II to break the emulsion and coagulate suspended matter was accomplished with 400 p.p.m. of lime and 60-70 p.p.m. $Fe_2(SO_4)_3$ in a mixing and settling period of 20 minutes and 2 hours, respectively. A clear supernatant liquor was obtained which showed a 71 to 85 percent reduction of the oxygen consumed and B.O.D., respectively, and a 9-fold decrease in the fish toxicity. The volume of sludge after 2 hours settling was 3% of the waste. Somewhat lower removal of impurities was obtained from the treatment of the Gunk-solvent cleaner waste (I), but at the expense of time and a greatly increased chemical dose,

i.e., 500 p.p.m of H_2SO_4 to break the emulsion and 60-70 p.p.m. $Fe_2(SO_4)_3$ plus 300 p.p.m. lime to coagulate and settle in a total treatment period of 3 hours. There was, however, a 20-fold decrease in fish toxicity.

The wastes from the use of steam-steam cleaner (V) were stable suspensions of what appeared to resemble aluminum paint. Compared to emulsion wastes the organic pollution was low. The oxygen consumed values of the waste were in the order of 1,000 p.p.m., of which only 10 to 15 percent could be attributed to cleaning compound. Thus the major portion of the O.C. may be attributed to dirt, grease and, probably largely the metal surface coating which had been removed from the aircraft. The B.O.D. of these wastes were less than that of weak sewage. The wastes contribute largely inorganic pollution due to residual alkalinity such as phosphates, silicates and metals. The use of steam compound No. 3347 produced a waste (VI) which was least toxic of all the wastes. It was 1/5 as toxic as Waste V, from the steam cleaner.

The addition of small quantities of iron salt and lime were sequestered by the steam cleaner wastes, and only when very large amounts of chemicals (H_2SO_4, $Fe_2(SO_4)_3$ and lime) were added did the suspensions coagulate. However, the very large volume of sludge produced (8 to 26%), precluded this method of treatment. Treatment of steam cleaner wastes by aeration or chlorination was effective in decreasing the toxicity to fish by over 50 per cent.

Waste VII, produced from the use of both Airmulso-solvent cleaner and steam-steam cleaner compound Formula C, was extremely high in organic pollutants and was the most toxic. Since prolonged storage had affected the physical, chemical and toxic properties of the raw waste, studies were conducted on a synthetic mixture prepared from the component cleaners in a

concentration comparable to the raw waste. The most effective treatment of the synthetic waste consisted of chlorination with 100 p.p.m. Cl_2, followed by pH adjustment to neutrality with about 600 p.p.m. H_2SO_4. The emulsion was thereby broken in less than 2 hours with the formation of about one volume of floating sludge for every 3 volumes of turbid undernatant. Although somewhat less than 95% reduction of the oxygen consumed value and the toxic components had occurred, the undernatant still contained an organic pollution equal to about twice that of a strong sewage. Further treatment for the removal of 50 percent of residual impurities was possible with lime and ferric sulfate coagulation.

Based on these laboratory studies and the characteristics of the cleaner compounds the following conclusions are indicated:

1. Emulsion-type cleaners produce rather stable emulsions of high organic load and high toxicity. With due consideration of the pollutional and toxic properties, discharge of the waste to sewage treatment plants or water courses without adverse effects is a possibility.
2. The Airmulso-solvent cleaner wastes are less toxic and can be more easily treated by chemicals than the Gunk-solvent cleaner wastes.
3. The wastes from steam-steam cleaner compounds produce stable suspensions of high alkalinity, but with low organic and low toxic properties. Consequently less dilution water would be required for their disposal by dilution, except as the residual sequestering properties of the diluted waste may have deleterious effects on sewage treatment or the receiving body of water. Chemical treatment is not indicated as effective for

these wastes.

4. Wastes produced from the use of a mixture of an emulsion cleaner with steam-steam cleaner compounds are most toxic and highest in organic properties. However, the Airmulso cleaner in combination with a steam cleaner compound can be chemically treated quite effectively.

5. Following the selection of the most satisfactory combination of cleaning procedure and cleaning agents from the standpoint of operation, decontamination, pollutional and toxic properties, and treatability, it would be desirable to make additional laboratory and pilot plant studies on treatment and disposal. Both cleaning and synthetic wastes should be included to cover the full range of waste concentrations and freshness of waste as it may affect treatment and disposal.